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(54) Manganese-zinc ferrites

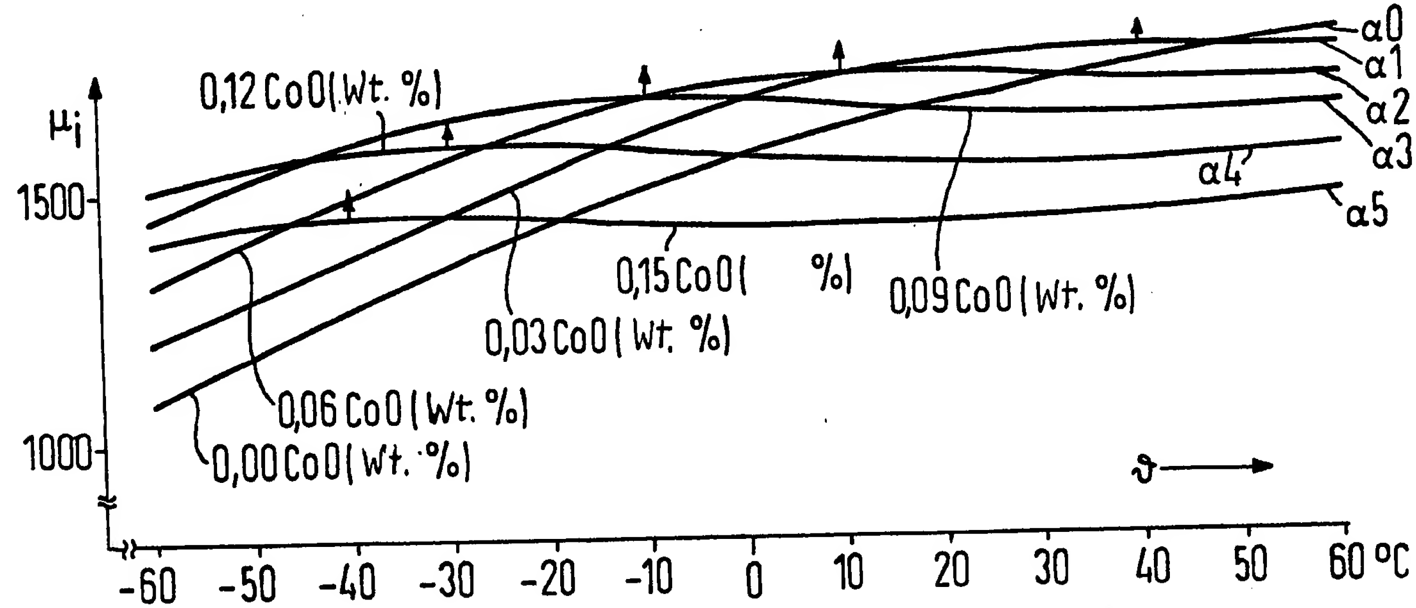
(57) A high or medium-permeability, low loss, calcium containing manganese-zinc ferrite with a given initial permeability temperature coefficient that is constant and positive or only fluctuates by a small amount around zero over a wide temperature range, has the following basic composition:–

49 to 55 mol % Fe_2O_3
0.2 to 5 mol % (SnO_2 and/or TiO_2)
remainder to 100 mol % MnO and ZnO combined with 0.03 to 0.4% by weight of CaO and a very small amount of CoO, in particular 0.02 to 0.5% by weight of CoO, the amount of CoO being chosen to match the theoretical Fe^{2+}-content level, which is controlled by the proportion of Sn, Ti and extra-stoichiometric iron present, in such a way that the desired temperature coefficient of the initial permeability μi is obtained.

GB 2 001 950 A

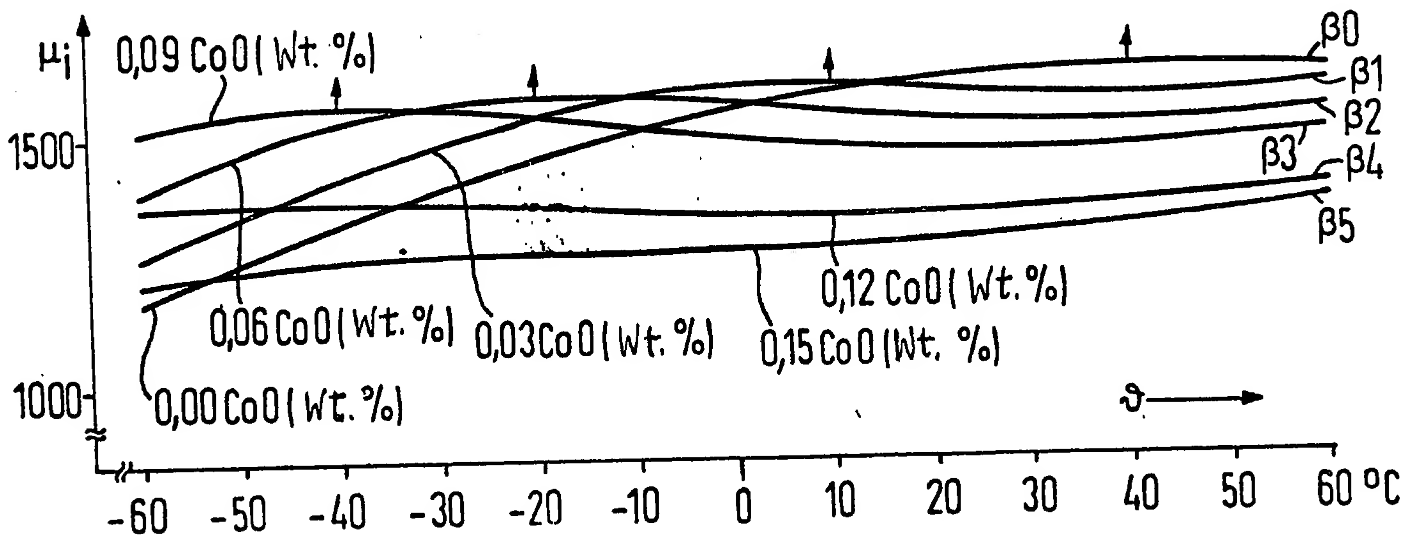
1/2

Fig.1



μ_i
1500
1000
0,12 CoO (Wt. %)
0,15 CoO (%)
0,09 CoO (Wt. %)
0,03 CoO (Wt. %)
0,06 CoO (Wt. %)
0,00 CoO (Wt. %)
α0
α1
α2
α3
α4
α5
ϑ
-60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 °C

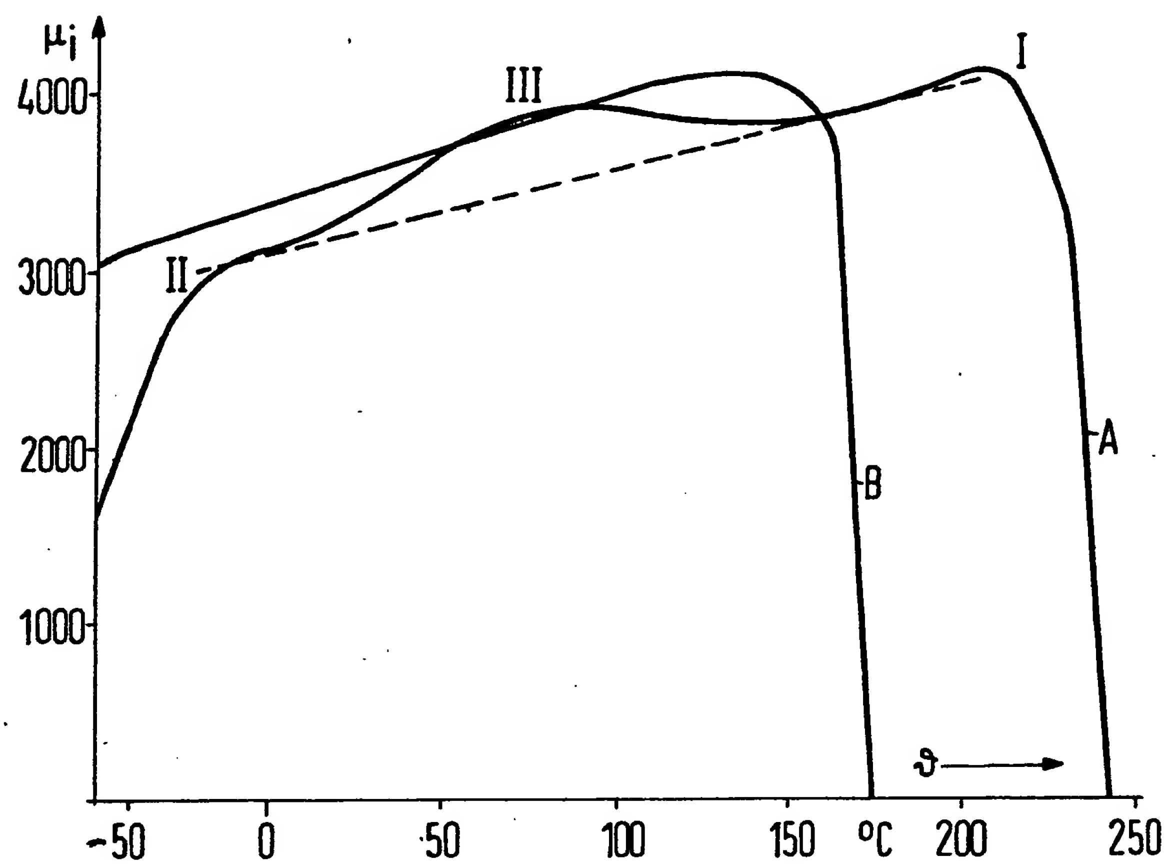
Fig.2



μ_i
1500
1000
0,09 CoO (Wt. %)
0,06 CoO (Wt. %)
0,03 CoO (Wt. %)
0,12 CoO (Wt. %)
0,15 CoO (Wt. %)
0,00 CoO (Wt. %)
β0
β1
β2
β3
β4
β5
ϑ
-60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 °C

2/2

Fig.3



μ_i
4000
3000
2000
1000
I
II
III
A
B
ϑ
-50
0
50
100
150
°C
200
250

SPECIFICATION

Manganese-Zinc ferrites

The present invention relates to manganese-zinc ferrites and to methods of producing them for the proper functioning of inductance coils in filter circuits comprising an inductance and a capacitance, the most important property of the inductive component, apart from quality, is the temperature coefficient of initial permeability of the material of the core which is usually a ferrite material. The temperature coefficient of inductance, which must be imversly related to that of the capacitance of the filter, determines the variation in frequency caused by the frequently inevitable temperature fluctuations, in accordance with the equation:

$$\omega\vartheta = 1/\sqrt{L_0(1+\alpha L\Delta\vartheta) \cdot C_0(1+\alpha_C\Delta\vartheta)}$$

where L_o and C_o denote the inductance and capacitance respectively at 0°C, α_L is the temperature coefficient of inductance and αc is the temperature coefficient of capacitance.

Only when $\alpha_L(\vartheta) = -\alpha c(\vartheta)$ can the filter frequency be kept approximately constant, i.e. the value maintained ω approximately equal to ωo where ωo is the frequency at the set temperature with the values L_o and C_o (0°C). In addition, ferrite materials having a temperature coefficient that only fluctuates around zero by a small amount are also of interest for filters, e.g. for use in oscillation circuits with mica capacitors for wide temperture ranges, e.g. in portable equipment, where $\alpha_L \approx \alpha c \approx 0$. The initial permeability/temperature (μ/ϑ) curve of manganese-zinc ferrites and therefore the associated losses of medium and high permeability ferrites depend upon magnetic saturation temperature response and upon the temperature effect of various energy parameters which are determined by the crystal anisotropy energy, magnetostriction and so on. By selecting suitable formulations and sintering conditions, these relationships can be so controlled that so-called secondary permeability maxima or bends occur in the $\mu(\vartheta)$ curve in certain temperature ranges. As a result, it is possible to obtain small, roughly constant temperature coefficients in certain temperature ranges above these singularities.

Thus, for example, by means of the Fe^{2+}-ion component of the ferrite lattice, the crystal anistopropy energy can be influenced, a specific amount of Fe^{2+}-ions being needed to lower the crystal anisotropy energy to zero at a specific temperature. The lower this temperature has to be (it is only above this zero point that the temperature coefficient is adequately small and satisfactorily controllable and the losses, particularly the hysteresis losses, are low) the more Fe^{2+}-ions have to be present in the ferrite lattice. The Fe^{2+}-ion component in the ferrite lattice can be controlled in two different ways, namely:

(1) through the total iron content, because any part of the totaliron ions which is in excess of an initial formulation of 50 mol % Fe_2O_3, becomes divalent when the ferrite is formed, because of charge neutrality (theoretically FeO Fe_2O_3 is formed), and

(2) as is described in German Patent Specifications Nos 1 300 860, 1 223 734 and 1 671 035, by incorporating tetravalent ions, such as, for example, Sn and Ti ions, which, with each tetravalent metal ion, render divalent, two iron ions which are initially trivalent, forming $Ti^{4+}Fe_2^{2+}O_4$ and $Sn^{4+}Fe_2^{2+}O_4$ in theory.

The crystal anisotropy can be considerably influenced and thus the initial permeability temperature coefficient controlled by ions other than $Fe2^{+}$-ions, namely by cobalt ions.

Each of these methods of controlling the temperature coefficient of the initial permeability, namely the use of an extrastoichiometric iron component, the substitution of part of the main components by tin and/or titanium, and the addition of cobalt, has already used to control the initial permeability temperature coefficient of manganese-zinc ferrites and results which are to some extent similar can be obtained with the different methods.

It is an object of the present invention to provide a Sn and Ti-substituted, high or medium-permeability, low-loose, calcium containing manganese-zinc ferrite with an initial permeability temperature coefficient which is substantially constant and positive, or which fluctuates only slightly about zero, over a wide temperature range, in particular between −60°C and +100°C, and which can therefore be used to produce components which are smaller than hitherto necessary, and which also contributes to a narrowing of the broad range of different types hitherto needed.

Surprisingly, it has been found that a suitable combination of the substitutes and additives already known and listed abov brings about results that are v n better than those hith rto known, and, in particular that a v ry small additi n f cobalt to a manganese-zinc ferrit already optimised as regards tin and titanium components allows the useful s rvice temperature rang to b furth r xtend d.

According to the invention, th re is provided a high r-m dium-perm ability, low-loss calcium-c ntaining manganese-zinc ferrit having a given initial p rmeability temp ratur coefficient that is constant and positive or fluctuates by only a small amount around z ro over a wid t mperature range, having a basic comp sition of:–

49 to 55 m l % Fe_2O_3,
0.2 to 5 mol% of SnO2 and/or TiO_2
remainder to 100 mol %, MnO and ZnO, and containing 0.03 to 0.4% by w ight of the basic composition of

CaO and a very small amount of CoO selected in dependence on the theoretical Fe^{2+}-content of the ferrite d termined by the proportion of Sn and/ r Ti and extra-st ichi metric iron, s as to produce the given initial permeability temperature coefficient.

The amount of CoO present is preferably from 0.02 to 0.5% by weight.

An advantageous method of producing a ferrite according to the invention comprises the steps of forming a starting mixture of:

49 to 55 mol % Fe_2O_3,
0.2 to 5 mol % ($SnO_2 + TiO_2$)
remainder to 100 mol %, MnO and ZnO
plus 0.02 to 0.5% by weight of the above components of CoO,

subjecting the mixture, if necessary to a prior heat treatment, grinding, adding 0.05 to 0.4% by weight of $CaCO_3$, pressing the ground material to form cores, heating the cores in a pure inert gas, in particular nitrogen, to the sintering temperature, in particular 1100 to 1300°C, sintering at this temperature in a nitrogen atmosphere containing oxygen and cooling in a nitrogen atmosphere under a decreasing partial pressure of oxygen.

The invention will be further described with reference to the drawings, in which:–

Figures 1 and *2* are similarly graphs on the initial permeability μ_i against temperature for two different basic ferrite formulations to show the effect of adding varying small amounts of CoO; and

Figure 3 is a graph of the initial permeability against temperature for two different ferrites according to the invention to illustrate the formation of secondary maxima.

The possibility of controlling the initial permeability temperature coefficient in accordance with the invention by the inclusion of suitable amounts of CoO is illustrated in Figures 1 and 2.

The basic formulation of the ferrite of Figure 1 is:–

52.95 mol % Fe_2O_3
32.60 mol % MnO
13.55 mol % ZnO
0.50 mol % SnO_2
0.40 mol % TiO_2

and that of the ferrite of Figure 2:–

52.43 mol % Fe_2O_3
32.62 mol % MnO
13.55 mol % ZnO
0.50 mol % SnO_2
0.90 mol % TiO_2

The effect of the CoO content on the relationship between temperature and initial permeability is shown. For every +0.01% by weight of CoO, or 0.016 mol % of CoO, the secondary permeability maximum (i.e. the shoulder on the $\mu_i(\vartheta)$ curve indicated by vertical arrows, is moved in the direction of decreasing temperature by about 7 to 10C°. To obtain the same movement of the secondary permeability maximum by the use of Fe^{2+}-ions would require about ten times as many Fe2+ ions as Co ions. It is thus possible to work in accordance with the invention with extremely low iron values and still obtain a kink in the $\mu_i(\vartheta)$ curve at a very low temperature. One advantage of this is that the disturbance phenomena occuring at high iron contents are avoided. An additional advantage of controlling the initial permeability temperature coefficient with the aid of Co ions lies in the fact that it is possible to work, not only with low iron contents, but also with low zinc contents i.e. at a higher Curie temperature, without the $\mu_i(\vartheta)$ curve sagging between the high and low temperature maxima. One reason for this may be a tertiary permeability maximum produced by the Co-ions as shown by ferrite A in Figure 3. This ferrite has been deliberately sintered so that the maximum, here at about +90°C, is clearly defined. Normally, however, the sintering will be carried out so that the ferrite has the curve shown by the broken line in Figure 3 where α_L is substantially constant over a wide temperature range. An example for this is ferrite B. Here α/μ_i is so small, at $0.4 \times 10^{-6}K^{-1}$, that the effective permeability μ_i can be doubled if the same capacitor is used in the filter as when previously using materials with $\alpha/\mu_i = 0.8 \times 10^{-6}K^{-1}$. In the present case, the smoothing of the $\mu_i(\vartheta)$ curve was effected by moving the maxima marked I, II and III namely the Hopkinson or primary maximum, the secondary maximum and the tertiary maximum, close together so that there is no longer any waviness in the $\mu_i(\vartheta)$ curve. The invention is illustrated by the following examples which illustrate in particular, the advantageous manner in which Co ions can be used in extremely small amounts to control the temperature coefficient of (Sn + Ti)- substituted manganese-zinc ferrites, and how, at the same time, very low losses and a low level of variation are obtained.

Example 1

Th following amounts of starting mat rials:–

51.5 mol % Fe_2O_3
31.0 mol % MnO
16.5 mol % ZnO
0.5 mol % SnO_2
0.5 mol % TiO_2
plus 0.2 % by w ight of CoO of the total w ight of the above materials

were mixed for 2 to 4 hours in distilled wat r in a ball mill, subj cted to a preliminary heat treatm nt at 850°C for one hour and then wet-ground for 2 hours whilst adding an am unt of $CaCO_3$ which will produce about 0.06 % by weight of CaO in the final product. Annular cores were pressed from the dried mixture at 1 kBar and were heated in pure nitrogen gas, sintered at 1250 to 1300°C in a nitrogen atmosphere containing 2 to 4 % by volume of oxygen and then cooled in a nitrogen atmosphere with a falling oxygen partial pressure, 0.8 % by volume of oxygen remaining at 1100°C and not more than 20 ppm of oxygen being present at below 900°C.

The effect of temperature upon the initial permeability μ_i is shown for this ferrite in Figure 3 (ferrite B). This highly permeable ferrite has a Curie temperature of 175°C and minimal loss coefficient over a wide temperature range together with a very constant positive temperature coefficient.

The technical characteristics of this ferrite are:

$\mu_i = 3500$
$\tan\delta/\mu_i = 1.5 \times 110^{-6}$ at 100 kHz
$= 0.8 \times 10^{-6}$ at 20 kHz
$= 0.5 \times 10^{-6}$ at 5 kHz
$\eta_B = 0.25 \times 10^{-6}$/mT at 100 kHz
$= 0.15 \times 10^{-6}$/mT at 20 kHz
$D/\mu_i = 2 \times 10^{-6}$, 2 h ... 20h, measured at 60°C.

The specific temperature coefficient α/μ_i is substantially constant and positive between −40 and +80°C and has a value of $(0.4 \pm 0.05) \times 10^{-6}K^{-1}$. Its value can also be adjusted to $(0.7 \pm 0.1) \times 10^{-6}K^{-1}$ for the same temperature range by the use of more severe oxidation during cooling.

A material of the same composition but without the addition of CoO in accordance with the invention, has with otherwise analogous electrical properties:

$\alpha/\mu_i = 0.2 \times 10^{-6}K^{-1}$ from 20 to 60°C and
$\alpha/\mu_i = (1.5 \text{ to } 2.5) \times 10^{-6}K^{-1}$ from 20 to −40°C, there thus being a sharp kink in the $/\mu_i(\upsilon)$ curve.

Example 2

A mixture of the following initial materials:–

50.55 mol % Fe_2O_3
32.25 mol % MnO
14.75 mol % ZnO
0.61 mol % SnO_2
1.84 mol % TiO_2
plus 0.05 % by weight of CoO

was subjected to the same preliminary treatment as described in example 1 and was combined with 0.1 % by weight of $CaCO_3$. Pressings made from this mixture were then heated to 1150 to 1200°C in pure nitrogen gas, sintered at this temperature in a nitrogen atmosphere containing 1 to 2 % of by volume of oxygen and then cooled in a nitrogen atmosphere with a falling oxygen concentration such that at 1000°C there was still 180 ppm of oxygen present and at 900°C only 10 ppm of oxygen. The medium-permeability ferrite obtained in this way had the following technical characteristics:

$\mu_i = 1600$
$\tan\delta/\mu_i = 1.1 \times 10^{-6}$ at 100 kHz
$= 6.7 \times 10^{-6}$ at 500 kHz
$\eta_B = 0.2 \times 10^{-6}$/mT (100 kHz)
$D/\mu_i = 3 \times 10^{-6}$ measured at 60°C, between 2 h and 20 h
$\alpha/\mu_i = (0.45 \pm 0.05) \times 10^{-6}K^{-1}$ from −20 to +80°C

A material of the same composition but without the proportion of Co has the following temperature coefficients with otherwise the same properties:

$\alpha/\mu_i = 0.6 \times 10^{-6}K^{-1}$ from 20 to 80°C
$\alpha/\mu_i = (1.5 \ldots 2.5) \times 10^{-6}K^{-1}$ from 20 to −40°C

Example 3

A low-permeability material with the following initial composition:

51.4 mol % Fe_2O_3
33.1 mol % MnO
14.1 mol % ZnO
0.5 mol % SnO_2
0.9 mol % TiO_2
plus 0.15 % by weight of CoO
and 0.1 % by weight of $CaCO_3$

was treat d essentially in th same manner as in example 1. Sintering for 1–2 hours to k place at 1150°C in a nitrogen atmosphere containing 1 % by volume of oxygen. Co ling was effected in a nitrogen atmosphere with the xygen content falling constantly to less than 20 ppm at 900°C.

The ferrite thus produced had the f llowing characteristics:

$\mu_i = 1200$
$\tan\delta/\mu_i = 1.5 \times 10^{-6}$ (100 kHz)
$= 5.0 \times 10^{-6}$ (500 kHz)
$= 15 \times 10^{-6}$ (800 kHz)
$\eta B = 0.4 \times 10^{-6}$/mT (100 kHz)
$D/\mu_i < 5 \times 10^{-6}$ at 60oC, between 2 and 20h
$\alpha/\mu_i = (0.75 \pm 0.05) \times 10^{-6}K^{-1}$ from −40 to +80°C

Without the added Co in accordance with the invention, at room temperature with otherwise similar properties there is a sharp kink in $\mu_i(\upsilon)$ curve with
$\alpha/\mu_i = 0.2 \times 10^{-6}K^{-1}$ from 20 to 60°C
$\alpha/\mu_i = (1.5 \ldots 2) \times 10^{-6}K^{-1}$ from 20 to −40°C

Example 4

Table 1 below shows with reference to substances 1 to 5 how the kink or maximum in the $\mu_i(\upsilon)$ curve is moved to lower temperatures for a given formulation by the addition of increasing amounts of CoO (see Figure 2) while at the same time extremely low loss coefficients are achieved in the low temperature range (and at temperature above the maximum temperature). Thus materials are obtained which can be used, for example, together with zero temperature coefficient capacitors. For practical purposes, the best materials are those marked β1 to β4. These are medium-permeability materials which can be used very satisfactorily up to frequencies of a few 100 kHz. β0 shows the properties of a material without the addition of CoO in accordance with the invention. The pressings used were made as in example 1. The cores were sintered at 1190°C in a nitrogen atmosphere containing 2.2 % by volume of oxygen. The cores were cooled in a nitrogen atmosphere with constantly decreasing oxygen partial pressure.

Example 5

Table 2 shows the properties of materials which also have a temperature coefficient that fluctuates around zero with a permeability level of about 2000. The powder and pressings were made as in example 1. The materials were sintered at 1200 to 1250°C in a nitrogen atmosphere containing 2 to 4 % O_2 and cooled in nitrogen with a decreasing oxygen content.

Table 1

Medium—permeability materials with extremely low losses at low and normal temperatures and a temperature coefficient that fluctuates around zero over a wide temperature range

Data Materials	CoO added (% by weight)	Main components (mol %)	Magnetic properties /ul	tan δ//ul 100kHz 20° (10-6)	tan δ//ul in min. 100kHz (10-6)	Temp. of loss min. (°C)	ηB;100kHz 10-6/mT (10-6)	D//ul 60°C, 2h-20h.	α// u_i /($10^{-6}K^{-1}$) 20. .80	20. .0	–20. .20	–40. .20
β 0	0	) Fe_2O_3 : 52.43	1500	1.3	1.3	+ 30	0.25	≦ 5	0.2	1.5	1.5	1.9
β 1	0.03	) MnO : 32.62	1490	1.25	1.0	+ 10	0.25	≦ 5	–0.003	–0.12	0.5	1.16
β 2	0.06	) ZnO : 13.55	1440	1.34	1.0	– 20	0.30	≦ 5	0.06	–0.5	–0.44	0.12
β 3	0.09	) TiO_2 : 0.90	1380	1.5	1.2	– 40	0.35	≦ 5	0.32	–0.54	–0.55	–0.5
β 4	0.12	) SnO_2 : 0.50	1275	1.6	1.2	– 40	0.40	≦ 5	0.5	–0.02	–0.22	–0.20
β 5	0.15	)	1220	1.6	1.4	– 30	0.63	≦ 5	1.2	0.5	0.35	0.40

Table 2

High—permeability materials with low loss coefficients over a wide temperature range and a temperature coefficient that fluctuates around zero over a wide temperature range

δ 0	0	) Fe_2O_3 : 50.55) MnO : 32.25	2100	1.2	1.2	+ 20	0.18	≦ 4	0.1	1.1	1.5	1.7
δ 1	0.05	) ZnO : 14.75	2000	1.1	1.0	–20	0.18	≦ 4	0.1	–0.1	0.3	0.8
δ 2	0.10	) TiO_2 : 1.63	1900	1.3	1.0	– 40	0.25	≦ 5	0.3	–0.1	–0.2	–0.1
δ 3	0.15	) SnO_2 : 0.82	1800	1.4	1.3	– 40	0.35	≦ 4	0.8	0.5	0.4	0.50

CLAIMS

1. A high or medium-permeability, low-loss calcium-containing manganese-zinc ferrite having a given initial permeability temperature coefficient that is constant and positive or fluctuates by only a small amount around zero over a wide temperature range having a basic composition of:

49 to 55 mol % Fe_2O_3,

0.2 to 5 mol % of SnO_2 and/or TiO_2

remainder to 100 mol % MnO and ZnO and containing 0.03 to 0.4% by weight of the basic composition of CaO and a very small amount of CoO selected in dependence on the theoretical Fe^{2+} – content of the ferrite determined by the proportion of Sn and/or Ti and extra-stoichiometric iron, so as to obtain the given initial permeability temperature coefficient.

2. A ferrite as claimed in claim 1 wherein the amount of CoO is from 0.02 to 0.4% by weight of the basic composition of the ferrite.

3. A ferrite as claimed in claim 1 substantially as hereinbefore described with reference to any of the examples.

4. A method of producing a ferrite as claimed in claim 1 comprising the steps of mixing the starting materials for the basic composition and from 0.02 to 0.5% by weight of the weight of the basic composition of CoO, grinding the mixture, adding an amount of CaCo3 which will produce from 0.03 to 0.04% by weight of the weight of the basic composition of CaO on sintering, pressing the mixture to form cores, heating the cores to a sintering temperature in a pure inert gas, sintering the cores at this temperature in an atmosphere of nitrogen containing oxygen, and cooling the sintered cores in a nitrogen atmosphere containing a continuously decreasing oxygen content.

5. A method as claimed in claim 4 wherein the mixed starting materials are subjected to a preliminary heat treatment before grinding.

6. A method as claimed in claim 4 or claim 5 wherein the cores are heated to the sintering temperature in an atmosphere of pure nitrogen..

7. A method as claimed in any one of claims 4 to 6 wherein the cores are sintered at 1100 to 1300°C.

8. A method of producing a ferrite as claimed in claim 1 substantially as hereinbefore described with reference to any of the examples.

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